SIMPLE NITROGEN OXIDES CHEMISTRY FOR INCORPORATION INTO LONG RANGE TRANSPORT MATHEMATICAL MODELS

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Acidic Precipitation in Ontario Study

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SIMPLE NITROGEN OXIDES CHEMISTRY FOR INCORPORATION INTO LONG RANGE TRANSPORT MATHEMATICAL MODELS

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DOWNSVIEW, ONTARIO

FOR:

ONTARIO MINISTRY OF THE ENVIRONMENT

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Summary

It has proved difficult to incorporate the chemistry of the nitrogen oxides into models of the long range transport of air pollutants, because of the complexity of the relevant chemical reaction schemes. This study was therefore undertaken to investigate the feasibility of representing the oxidation of the nitrogen oxides by a first order scheme, viz

$$NO \xrightarrow{k_1} NO_2 \xrightarrow{k_2} \text{Nitrates}$$

A survey of the recent literature revealed that this has not yet been done, so an analysis of a body of smog chamber data was undertaken. It proved that a first order reaction scheme represents the temporal behaviour of NO and NO_2 with adequate accuracy, and it was possible to parameterise the resulting pseudo-first order rate constant, k_2, in terms of the surrogates, ozone and hydrocarbons. Since k_1 is much larger than k_2, the first step may normally be assumed to be instantaneous.

Inspection of the few available studies of NO_2 oxidation in the atmosphere reveals that the first order rate constants derived from them cluster around the minimum value found in smog chamber experiments, i.e. 0.0025 min^{-1}. This indicates that if average effects are to be modelled, use of an average rate constant is satisfactory, since the rate constant in the atmosphere is apparently not subject to large variations. This average may be derived directly from field studies, or by exploiting the approximately constant ratio between the oxidation rates of NO_2 and SO_2. The atmospheric oxidation rate of SO_2 is much better established than that of NO_2.

The partitioning of the "nitrate" products between inorganic (mainly HNO_3) and organic (peroxyacetyl nitrate, PAN) was investigated by computer simulation, because of the sparsity of experimental data, and a recommendation made regarding the time evolution of the ratio HNO_3/PAN, which recognizes the significant temperature dependence of the rate of dissociation of PAN to regenerate NO_2 and peroxyacetyl radical.

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SIMPLE NITROGEN OXIDES CHEMISTRY

1. Introduction

Long range transport of atmospheric pollutants is currently the subject of intensive study by numerous groups in Canada and elsewhere. Mathematical models describing transport and diffusion over temporal and spatial scales of hours and hundreds of kilometers have been developed. In order to consider adequately the effects of pollutant emissions, chemical and physical transformation processes as well as atmospheric removal mechanisms need to be included in model development. Most long range transport models currently in practical use are based on Lagrangian formulations which are limited in that only first order transformation processes can be included. Eulerian formulations, although they allow for inclusion of complex transformation processes, are extremely difficult to solve and require large computer resources.

The Ontario Ministry of the Environment has developed a long range transport model which includes first order mechanisms for sulfur transformation and deposition processes. It is recognized that nitrogen oxides also play an important role in the long range transport of atmospheric pollutants, however, the atmospheric chemistry of nitrogen oxides is complex and has not yet been included in the MOE model. This report presents the results of a study conducted by Concord Scientific Corporation to determine the feasibility of incorporating simple nitrogen oxide chemistry into the MOE model, and, if this is possible, formulating how it should be done.

The current scientific literature was surveyed to include pertinent laboratory and field study results on nitrogen oxide atmospheric reactions as well as mathematical modelling simulations. These results were considered from the point of view of the suitability of the use of simple first order reactions of nitrogen oxides to describe their atmospheric chemistry and how the first order rate constants could be parameterized in terms of variables which are routinely measured.

The formal representation of the atmospheric reactions of nitrogen oxides is:

$$NO \xrightarrow{k_1} NO_2$$

$$NO_2 \xrightarrow{k_2} \text{Products}$$

Where k_1 and k_2 are pseudo-first order rate constants and "products" includes organic and inorganic nitrates. Both k_1 and k_2 are examined for both goodness of fit as a first order rate constant and their dependencies on other parameters of the reaction system.

In this report, Section 2 describes information obtained from the literature on the way in which NO_x has been included in transport models, and also includes a description of experimental measurements (field and laboratory) of the conversion reactions of NO and NO_2. In Section 3 the accuracy of a first order description of these reactions is investigated, and the resulting first order rate constants parameterized. An estimate of the night time rate constant is given, and in Section 4 the time and temperature dependence of

the product distribution of the NO_2 oxidation are derived.

The theoretical rationale behind the empirical work of Section 3 is briefly outlined in Section 5, and the internal consistency of the various approaches demonstrated. The conclusions of the preceeding sections are summarized in a series of recommendations in Section 6.

2. Literature Survey

A review of the recent literature and discussions with key researchers in the field shows that very few long range transport models incorporate NO_2 chemistry. Demerjian (1981) reports that there is no regional scale transport model in current use, which incorporates proper atmospheric photochemistry, though Demerjian, at the U.S. Environmental Protection Agency (EPA), is working on the development of one. This model is, however, based on an Eulerian formulation and will require several years to develop.

Rodhe et al (1979) incorporated a 20 reaction scheme into their multi-day transport model. The maximum rate of NO_x transformation was about 13% hr^{-1} compared with about 1% hr^{-1} for SO_2.

Levine (1980) described how a conventional 30 species, 45 reaction scheme was condensed to a 15 species, 45 reaction surrogate scheme for incorporation in a transport model. The surrogate reproduced the results of the full scheme very well, at a saving in computer time of approximately 60 - 70%. Working on a similar time scale (24 hours), Hov and Isaksen (1980) used a full reaction scheme described by Derwent & Hov (1980).

Stewart and Liu (1980) incorporated a kinetic module into their model of the Oak Creek Power Plant in Wisconsin and of the Widows Creek Power Plant in Alabama. Their reaction scheme grouped together hydrocarbon reactions for simplification. This method, known as the Carbon Bond Mechanism, has been validated in smog chamber simulations (Whitten and Hogo, 1977).

Drivas et al (1980) described a model designed to estimate plume visibility. First order transformation of SO_2 was incorporated, but NO_x chemistry was limited to the photostationary state between NO, NO_2 and O_3. A similar treatment of NO_x was featured in the plume model of Melo, Lusis and Stevens (1977).

Two recent papers (Bergstrom et al, 1980, and Blumenthal et al, 1980) describe modelling of a power plant plume in clean background air (i.e. no hydrocarbons). Here a set of 9 reactions among NO, NO_2, O_3, O_2, SO_2, OH, H_2O and O('D) was found to be adequate.

Of interest, although it is not strictly a transport model, and does not include NO_x kinetics, is the model described by Benkley and Mills (1980). Designed to describe long term (approximately monthly or longer) average air quality over a large area, this model describes NO_x chemistry in terms of an instantaneous partition between NO and NO_2. At present, the further oxidation of NO_2 is not included, but the authors state that this can readily

be done.

The above studies do not address the question of whether NO_x chemistry can be described in terms of first order kinetics. The literature was therefore, surveyed further in order to examine reported results on NO_x reactions both in the laboratory (smog chambers) and in the field. There is now a considerable body of information on smog chamber experiments (e.g. Pitts et al 1977, Pitts et al 1979, Spicer et al 1980, Spicer 1979, Akimoto et al 1979, 1980 a, b, Sakamaki et al 1980, Carter et al 1979), but very much less from atmospheric measurements. The group at Battelle Columbus laboratories (Spicer 1979, Spicer et al 1980) have reported results on the Boston urban plume, and on the Philadelphia urban plume (Spicer & Sverdrup 1979) and were able to fit the disappearance of NO_2 to a first order rate law. Forrest el al (1980) measured the rate of conversion of NO to nitrates in the Cumberland Power Plant Plume and found that it lay generally in the range 3 - 12% hr^{-1}. Hegg and Hobbs (1979), however, reported a conversion rate of only 0.3% hr^{-1}. It is an unfortunate fact that good quality measurements of nitrate concentrations are still difficult to make (Spicer 1980, Stedman 1980) and as a further complication, the conversion of NO to NO_2 in the early stages of plume development is limited by the rate at which ozone is mixed into the plume (see, for example, Melo 1980). This latter fact could well explain the low conversion rate observed by Hegg & Hobbs. It seems clear from the available literature that the oxidation reactions of NO to NO_2 and NO_2 to nitrates are, in the absence of other limiting factors, more rapid than observed by them.

3. Derivation of First Order Rate Constants

Initially a full, formal analysis of a reasonably complete reaction scheme (see for example, Derwent and Hov 1980) was considered using all reasonable simplifying techniques and assumptions. This has been done for the atmospheric oxidation of SO_2 by Moller (1980), who was able to show that the reaction between SO_2 and OH was dominant. Based on the current understanding of the atmospheric chemistry of NO_x it is reasonable to assume that the major pathway for the oxidation of NO_2 to HNO_3 is reaction with the OH radical. However, other channels are also open for the reaction of NO_2, e.g. the formation of PAN and other organic nitrates. Furthermore, it is still not possible to relate the OH concentration to the composition of the reacting air mass (or to the concentration of other surrogate observables) without carrying through the kinetic analysis.

An attempt was made to carry out this analysis. However, even an abbreviated mechanism for the photochemistry of polluted air consists of possibly 50 or more reactions, so the effort was soon abandoned as being too complex for this study. No doubt the same conclusion has been reached by many other workers in the field as evidenced by the absence of NO_x chemistry in most models.

Accordingly an empirical approach was adopted with the objective of answering two questions:

1. Can the transformation reactions of NO and NO_2 be described with adequate accuracy (i.e. within a factor of 2 or 3) by means of

first order kinetics?

2. If this can be done, can the resulting apparent first order rate constants be parameterized in terms of readily observable quantities, to allow their incorporation into computer models.

3.1. Verification of First Order Kinetics

Approximately thirty smog chamber runs were analysed in terms of first order kinetics. Where possible, the disappearance of NO, the initial appearance of NO_2 and its subsequent disappearance were all processed using a least squares fitting procedure, seeking agreement with the scheme

$$NO \xrightarrow{k_1} NO_2 \xrightarrow{k_2} \text{Nitrates}$$

The reactions were all followed for at least one half life, and usually for two or more half lives. Sample results are shown graphically in Figure 1 and Figure 2. Figure 1 includes the two cases which were respectively the best and worst fits of experimental data to first order kinetics, as measured by the standard deviation of the fit. The standard deviations were 0.022 and 0.385 (correlation coefficients of 0.985 and 0.958), indicating that a first order formulation is adequate for describing these oxidation reactions. This is in accord with the findings of Spicer et al (1980) on smog chamber results and Spicer (1979) on an urban plume.

3.2. Parameterisation of Rate Constants

3.2.1. NO Oxidation (k_1)

The dependence of k_1 on the following factors was considered:

i) Hydrocarbon concentration

ii) Carbon monoxide concentration

iii) Ozone concentration

iv) Relative humidity

v) Temperature

Variation of k_1 with all of these was found, but no clear correlation emerged. However, this apparently negative finding is of no consequence for two reasons:

i) On the time scales of interest in long range transport models (typically 6 hour time steps) the conversion of NO to NO_2 will usually be close to completion before the model gets going, i.e. the initial conditions to be used are:

$$(NO) = 0$$
$$(NO_2) = (NO_2)_o + (NO)_o$$

This clearly depends on the ambient oxidant concentrations particularly ozone, but is in line with the observations of Spicer (1980b) on the Boston urban plume, and is supported by the data of Stewart & Liu (1980) Further, k_1 values derived in this work were

about 5 to 15 times as large as the k_2 values. This means too, that any resulting overestimate in the nitrate concentrations early in a model run will be small.

ii) If short time scales are to be considered, it is well established (eg Melo, 1980, Forrest et al, 1980) that the dominant oxidation pathway for NO is its reaction with O_3, and the rate of this process is determined by the rate at which background O_3 is mixed into the plume. This is the reason for the well documented ozone deficit in the early stages of plume development.

3.2.2. NO_2 Oxidation (k_2)

It has been possible to parameterise k_2 at various levels of sophistication, as is described below. The choice of level is determined by the type of effect being modelled. For example, long term (seasonal or annual) effects can satisfactorily be handled by one average rate constant, while modelling of a single event requires that the rate constant used be tailored to the conditions pertaining to that event.

3.2.2.1. Long Term Average Value for Rate Constant k_2

Although good quality field measurements of NO_2 conversion rates are scarce, an average value can be taken from the work of Spicer and co-workers. They report a rate constant value of 0.10 ± 0.05 hr^{-1} for the Los Angeles area (Spicer 1977), an average of 0.17 hr^{-1} for the Boston urban plume (Spicer et al 1979), and a lower limit of 0.12 hr^{-1} for the Philadelphia plume (Spicer

Sverdrup 1979). Of these, the Boston results are considered the most reliable, since these experiments were designed to measure the transformation rate (unlike the Los Angeles experiments) and since the plume was carried out over the Atlantic ocean, avoiding the subsequent mixing in a NO_x from other sources, as probably happened with the Philadelphia plume, leading to an underestimate of the transformation rate of NO_2.

These rate constants are daytime values, taken in August during the morning and early afternoon. The value of k_2 obviously depends on the solar intensity at any given time, but it does not drop to zero at night, since there is a dark reaction, which will be discussed later.

3.2.2.2. Value of Rate Constant k_2 Related to SO_2 Oxidation Rate

The dominant pathways for the homogeneous oxidation of SO_2 and NO_2 are both by reaction with OH:

$$SO_2 + OH \longrightarrow HSO_3 \qquad k = 1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$NO_2 + OH \longrightarrow HNO_3 \qquad k = 1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

(Derwent & Hov 1980). On this basis one would expect the rate of NO_2 oxidation to be ten times faster than that of SO_2. However atmospheric measurements have resulted in ratios of 3 (Forrest, Garber and Newman 1980), 3 (combining the OECD results on NO_2 of Ohmstedt and Rodhe, 1978, with those on SO_2 of Eliassen 1978) and 3 to 10 (Richards et al, 1980). In a smog chamber, Spicer (1980) reports ratios for two experiments of 9 and 65.

Disregarding the last two values, since they were not obtained in the field, it seems that one can obtain the rate constant for NO_2 oxidation

by multiplying the corresponding rate constant for SO_2 by a suitable factor, which lies between about 3 and 10, with 4 probably being the best value. This procedure is in accordance with the suggestion of Richards et al (1980), who felt that conversion rates of NO_2 are, as yet, difficult to measure satisfactorily, and should be obtained in this way.

The appropriate SO_2 rate constant can be obtained in one of three ways:

i) By taking an average value from the literature. SO_2 conversion rates have been much more extensively measured than have NO_2 rates, and have been reviewed recently (see eg. Wilson & Gillani 1979, 1980, Newman 1980, Alkezweeny 1980). Although early reports disagreed widely, it would appear that this rate would typically be 0.5 to 1% hr^{-1}, for a 24 hour average value, or 1 to 4% hr^{-1} for daytime in polluted air.

ii) By actual measurement of the SO_2 conversion rate in the region and under conditions which are to be modelled.

iii) By using a parameterisation for the SO_2 rate, such as that proposed by Gillani et al (1980). The give:

$$\text{Rate} = 0.03\ R.H.\ (O_3)\ \%\ hr^{-1}$$

Where R = Solar raditation intensity (kWm^{-2})

H = Mixing height (m)

(O_3) = background ozone concentration (ppm)

It has not yet been established whether or not this parameterisation is site specific (M. Lusis - private communication).

There are further caveats to the approximation that the NO_2 conversion rate is more rapid by a constant factor than the SO_2 conversion rate, and a pointer to some of these is the fact that the ratio of the rate constants for the reaction of the two species with OH is 10, whereas the ratio of the transformation rates, as measured in the field is about half of that. This suggests that there is at least one other significant channel for the oxidation of SO_2, including the possibility of heterogeneous reactions.

In fact, Levine (1980) has found that:

$$SO_2 + O \longrightarrow SO_3 \quad (k = 5.7 \times 10^{-14}\ cm^3\ molec^{-1}s^{-1})$$

can be important whereas

$$NO_2 + O \longrightarrow NO_3 \quad (k = 2 \times 10^{-12}\ cm^3\ molec^{-1}s^{-1})$$

is significantly slower than

$$NO_2 + O \longrightarrow NO + O_2 \quad (k = 9.3 \times 10^{-12}\ cm^3\ molec^{-1}s^{-1})$$

thus increasing the SO_2 rate relative to the NO_2 rate in the presence of oxygen atoms.

On the other hand, under conditions of relatively high hydrocarbon concentration, a large proportion of the NO_2 will react to form organic nitrates, particularly PAN. This is presumably the reason for the faster oxidation rates for NO_2 relative to SO_2 obtained by Spicer, as quoted above, since his experiments were carried out under conditions of relatively high hydrocarbon concentration.

It would seem that the best option available for the determination of the rate constant for SO_2 oxidation is to measure it on site under the

conditions of interest. Unfortunately this is also the least practical alternative.

3.2.2.3. Parameterisation of k_2

For the modelling of relatively long term average effects the procedure described under (i) above should prove to be accurate enough (procedure (ii) is not practical, while (iii) is not yet proven). However, if specific episodes are to be modelled a more reliable estimate of k_2 is required. For this reason a comprehensive investigation of the parameterisation of k_2 was carried out, based on the rate constants derived from smog chamber work. Such field measurements of k_2 as do exist were checked for consistency with the result obtained.

Spicer (1980) found a good linear correlation between k_2 and the ratio $^{(HC)}o/(NO_x)_o$, where these are the initial concentrations of non-methane hydrocarbons and NO_x respectively. However, he worked with hydrocarbon mixtures of constant composition, designed to simulate the polluted urban atmosphere.

In this study, encompassing a range of hydrocarbon compositions, a better agreement was found (correlation co-efficient of 0.822 compared with 0.726) if k_2 is correlated with $(HC)_o$ rather than $^{(HC)}o/(NO_x)_o$. Here the hydrocarbon concentrations were adjusted for reactivity, such that

$$(HC) = (\text{unsaturated}) + (\text{branched, saturated}) + 1/3\ (\text{linear, saturated})$$

The factor of 1/3 was derived empirically, but is in rough agreement with the factor of 1/6 derived by Miller and Joseph (1976). The two correlations for k_2 are displayed in Figures 3 and 4.

Unfortunately a relationship between k_2 and hydrocarbon concentration is probably not useful to the modeller, since (HC) is not routinely measured, and when it is, it is normally reported as ppmC, which does not allow an adjustment for reactivity, since the composition of the mixture is not known.

Accordingly, a correlation was sought between k_2 and the final, steady ozone concentration produced, since ozone production is often used as a basis for measuring hydrocarbon reactivity. The result is shown graphically in Figure 5, and the correlation coefficient obtained was 0.820. Also included in Figure 5 are such field measurements as are available. The distinction between this parameterisation, and that of Gillani et al (1980) for SO_2 should be emphasized. They related the conversion rate to the background ozone concentration, being a measure of the reactivity of the ambient air. In this study k_2 is correlated with the final, approximately steady ozone concentration produced in the mature plume, since this measures the reactivity of the initial hydrocarbon mixturein the ambient air. Clearly, since the two are essentially measuring the same thing, there should be a means of converting from one basis to another. However, it appears that no experiments have yet been performed which will allow this to be done.

Other factors apart from reactive hydrocarbon concentrations which could affect the value of k_2 are temperature, relative humidity, and intensity of solar radiation and the proper inclusion of these into the parameterisation must be considered.

Simulation studies by Bottenheim et al (1977) revealed an almost neglible effect of temperature changes on k_2, while Carter et al (1979) measured much larger effects in a smog chamber. However, Pitts (1981), pointed out that changing the temperature in a smog chamber could cause effects due essentially to changes in the effects at the walls. Therefore, since the activation energies of the reactions involved in NO_2 removal are small, the assumption is made that changing the temperature, within the normal range encountered in the atmosphere, does not affect k_2.

The effect of temperature changes can not be ignored completely, however, since they do affect the relative distribution of products. This aspect will be considered separately.

Effects of changes in relative humidity on the oxidation rates of NO_x have been reported (Spicer 1980 a, Sakimaki et al 1980), but Pitts (1981) has indicated that changes in relative humidity in the smog chamber at the University of California at Riverside seem to produce their major effects through changes in the wall effects. In line with this, the suggestion has been made (Calvert 1981) that the largest effect of relative humidity changes in the atmosphere could be due to altered deposition rates (e.g. into clouds and mist, or onto the ground). However, the possibility should not be ignored of water complexation of free radical species such as OH, RO_2, etc. similar to the complexation of HO_2 which has previously been reported. This would certainly affect the reactivity of such species.

Because of the uncertainties surrounding this topic it is difficult to draw any firm conclusions, but an examination of the reactions which lead

to the production of O_3 suggests that a correlation of k_2 with O_3 should automatically include at least part of the effect due to changes in relative humidity. This study does not, therefore, attempt to include relative humidity further in the parameterisation of k_2.

The oxidation reactions of the nitrogen oxides are largely photochemical, and their rates are therefore, affected by the intensity of solar radiation. It has, however, been pointed out (Bottehnheim 1981) that the final ozone concentration attained by a polluted parcel of air is directly determined by the radiation intensity (this is clearly demonstrated in the simulation work of Bottenheim et al (1977)), which means that basing k_2 on final ozone concentration implicity allows for variations in solar intensity.

Another possibility to be considered is possible interactions between NO_2 and SO_2. Calvert et al (1977) have concluded that direct reactions between NO_2 and SO_2 are not of atmospheric importance, and SO_2 will be unable to affect NO_2 reactions by competition, since the rate of the SO_2 reaction with important intermediates, such as OH, is much lower than that of NO_2. Thus, the rate constant k_2 does not depend on SO_2 concentration, as is borne out by the work of Wallace et al (1980). Perhaps more important is the fact that they find the production of ozone is not changed by the presence of SO_2, indicating that the correlation between k_2 and O_3 remains valid in mixtures containing SO_2.

The possibility was raised by Calvert (1981) that a linear correlation between k_2 and (O_3) may fail under conditions of high $^{(HC)}o/(NO_x)_o$ because the channel leading to organic nitrates will be considerably enhanced. In

Figure 5 three experiments using unusually high ratios of $(HC)_o/(NO_x)_o$ (4 or larger, where $(HC)_o$ is the reactivity adjusted concentration as described above) do indeed lie well above the best fit line (the points are circled). However, it is difficult to say whether or not this is statistically significant. Further, it is probable that only a most unusual set of circumstances involving a strong source of hydrocarbons, without emission of NO_x (a possible example might be an oil refinery with strong fugitive emissions) will result in such a high ratio in the atmosphere, thus this effect is not considered further.

3.2.2.4. The Dark Reaction of NO_2

As mentioned above, the oxidation of NO_2 still proceeds, although at a much slower rate, in the dark. This is believed to be due to the sequence:

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \qquad k_3 = 3.4 \times 10^{-17}\ cm^3\ molec^{-1}s^{-1}$$

$$NO_2 + NO_3 \longrightarrow N_2O_5 \qquad k_4 = 2.6 \times 10^{-12}\ cm^3\ molec^{-1}s^{-1}$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3 \qquad k_5 = 1.0 \times 10^{-16}\ cm\ molec^{-1}s^{-1}$$

Insertion of approximate concentrations, eg.

$$(O_3) = (NO_3) = 100\ ppb$$
$$(NO_3) = 10^{-5}\ ppb$$
$$(N_2O_5) = 0.1\ ppb$$
$$(H_2O) = 1.7 \times 10^4\ ppm\ (40\%\ RH)$$

indicates that reaction between NO_2 and NO_3 is rate determining, being slower than the next slowest, the reaction between NO_2 and O_3, by 100 times, with an

apparent first order rate constant given by

$$k = k_4 (NO_3)$$
$$= 2{,}6 \times 10^{-12} \times 2{,}4 \times 10^{5} \times 60$$
$$= 3.7 \times 10^{-5} \text{ min}^{-1}$$

3.2.2.5. Loss of NO_x By Deposition

Consideration of deposition rates of NO_x and products is not within the scope of this study, but it should be pointed out that a depsoition velocity of 0.5 cm s^{-1} for NO_2, coupled with a mixing height of 1 km corresponds to a first order removal process, with a rate constant of 3×10^{-4} min^{-1}. This is not competitive with the daytime chemical conversion rates of NO_x, but will compete with the night-time rate if a deposition velocity of 0.5 cm s^{-1} is applicable.

4. Products of NO_2 Oxidation

The products of the oxidation of NO_2 are nitrates, either inorganic (eg. HNO_3, NH_4NO_3, etc.) or organic (eg. PAN, PPN, etc.). The most important of these are HNO_3 and PAN, and k_2 therefore consists of two main parts, corresponding to the two channels. However, the picture is complicated by the fact that there is an appreciable back reaction of PAN to peroxyacetyl radical and NO_2, i.e. the reaction scheme is

$$NO_2 \xrightarrow{k_{2a}} HNO_3 \qquad (2a)$$

$$\xrightarrow{k_{2b}} PAN \qquad (2b)$$

$$\xleftarrow{k_{-2b}}$$

The rate of dissappearance of NO_2 is then

$$-\frac{d\,(NO_2)}{dt} = (k_{2a} + k_{2b})\,(NO_2) - k_{-2b}\,(PAN)$$

$$= \left\{ k_{2a} + k_{2b} - k_{-2b}\,\frac{(PAN)}{(NO_2)} \right\} (NO_2)$$

If NO_2 oxidation is treated in terms of first order kinetics the apparent first order rate constant, k_2, is then given by

$$k_2 = \left(k_{2a} + k_{2b} - k_{-2b}\,\frac{(PAN)}{(NO_2)}\right)$$

This means that k_2 should actually be time-dependent, by virtue of the time dependent ratio $(PAN)/(NO_2)$, which suggests that such a detailed examination of the transformation of NO_2 to products is not appropriate in the framework defined by forcing the NO_x chemistry to obey first order kinetics.

Instead, the situation can be described in terms of a partition ratio

$$R = \frac{(HNO_3)}{(PAN)}$$

where R is also equal to k_{2a}/k_{2b}, if the reaction scheme is simplified to

$$NO_2 \xrightarrow{k_{2a}} HNO_3 \qquad (2a)$$

$$\xrightarrow{k_{2b}} PAN \qquad (2b)$$

To allow for the dissociation reaction of PAN, R is made time dependent, and it must also be temperature dependent since the dissociation of PAN has an appreciable activation energy (Hendry & Kenley 1977).

Values for R were obtained by computer simulation of the scheme using the known Arrhenius form for k_{-2b} (Hendry & Kenley 1977) and varying k_{2a} and k_{2b} over a wide range while ensuring that the net rate of disappearance of NO_2 remained in agreement with the rate constants derived in Section 3.1. The resulting sets of values of R for different k_{2a} and k_{2b} were then normalized by means of a multiplicative constant, such that the 298K, 400 minute values coincided. The average R value for each temperature time point is reported in Table 1. The maximum deviation within a set of R values being averaged was $\pm$ 25% over a wide range of choices of k_{2a} and k_{2b}.

5. Rationale for Dependencies of k_1 and k_2

As described in Section 3 an attempt was made to carry out a full kinetic analysis to derive a detailed relationship between k_1 and k_2 and the various parameters of the reacting air mass, but this proved to be impractible. However, the various dependencies of k_1 and k_2 can be rationalized in outline as follows:

5.1 Conversion of NO to NO_2 (k_1)

The main oxidizing agents responsible for the conversion of NO to NO_2 are O_3, HO_2 and RO_2 (eg. Demerjian et al 1974, Derwent and Hov 1980). The production of HO_2 involves OH and CO via

$$OH + CO \longrightarrow CO_2 + H$$

$$H + O_2 \longrightarrow HO_2$$

while the alkyl peroxy radical is typically produced by

$$RH + OH \longrightarrow R\cdot + H_2O$$

$$R\cdot + O_2 \longrightarrow RO_2$$

The rate constants for the oxidation reactions are

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad k = 25.2 \text{ ppm}^{-1} \text{ min}^{-1}$$

$$NO + HO_2 \longrightarrow NO_2 + OH \qquad k = 1{,}2 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$$

$$NO + RO_2 \longrightarrow NO_2 + RO \qquad k = 1 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$$

However, typical concentrations of the three species in polluted air are expect to be

$$O_3 \simeq 100 \text{ ppb}$$
$$HO_2 \sim 0.01 \text{ ppb}$$
$$RO_2 \lesssim 0.01 \text{ ppb}$$

The concentration of O_3 is therefore larger than that of the other two by about a factor of 10^4, which explains why its reaction is dominant in spite of the smaller rate constant.

5.2. Conversion of NO_2 to Products (k_2)

The major routes for oxidation of NO_2 are

$$NO_2 + OH \longrightarrow HNO_3$$
$$NO_2 + RO_2 \longrightarrow RO_2NO_2$$

where the main peroxy radical will usually be peroxyacetyl, giving PAN as product. Production of the two free radical species is by photochemical reaction involving such species as water, ambient hydrocarbons, etc. It is therefore, not surprising that such factors as hydrocarbon concentration, relative humidity, solar radiation, etc. must be considered in the determination of k_2.

It is interesting to note that our results derived from about 30 smog chamber experiments indicate a minimum value of k_2 of approximately 0.0025 min^{-1}, even for low hydrocarbon concentrations. If this is combined with the rate constant for reaction between OH and NO_2 (1.1×10^{-11} cm^3 $molec^{-1}s^{-1}$, Anastasi et al, 1976) an OH concentration of about 3.5×10^6 radicals per cubic centimetre is obtained, which is in the range of currently accepted values. Further, a figure of 0.0025 min^{-1} is in good agreement with the mean value obtained by Spicer (1980) for the Boston urban plume (0.17 hr^{-1}) and also with the procedures suggested for obtaining k_2 from SO_2 conversion rates. i.e. taking the average SO_2 oxidation rate in polluted air to be 4% hr^{-1}, with NO_2 rate = 4 x SO_2 rate. This gives an NO_2 rate constant of 0.16 hr^{-1}, or 0.0027 min^{-1}.

6. Recommendations

6.1. Conversion of NO to NO_2 (k_1)

As derived in this work, the rate constant for conversion of NO to NO_2 is typically 5 to 15 times larger than the rate constant for conversion of NO_2 to products. Therefore, on the time scale envisaged for this work, the reaction

$$NO \longrightarrow NO_2$$

can be assumed to be instantaneous.

If shorter time scales are to be considered (eg. total time of about 5 hours or less) the rate of the above reaction is limited by the rate at which ozone can be mixed into the plume, and this would have to be modelled as a problem in atmospheric dispersion.

6.2. Conversion of NO_2 to Products (k_2)

Three different approaches are proposed, depending on the temporal and spatial resolution and the degree of sophistication of the model.

Procedure I

The rate constant k_2 is set equal to the mean value obtained by Spicer (1979) for the Boston urban plume, i.e.

$$k_2 = 0.17 \text{ hr}^{-1}$$
$$= 0.0028 \text{ min}^{-1}$$

This is a summer, daytime value, and should be scaled down for conditions of lower solar intensity, using a linear dependence of k_2 on solar intensity (see, for example, Jones et al., 1981).

Under night-time conditions the value to be used is as derived in Section 3.2.24., i.e.

$$k_2 = 4 \times 10^{-5} \text{ min}^{-1}$$

Procedure II

The value of k_2 is taken to be 4 times as large as the rate constant for transformation of SO_2 to sulphates. Ideally the SO_2 rate constant should be measured at the site and under conditions where k_2 is required. If this is not possible, the SO_2 conversion rate can be assume to have a daily average of 4% hr^{-1} for polluted air, or 1% hr^{-1} for clean air. As mentioned in Section 5 this method results in the same value for k_2 as does Procedure I. Again, k_2 should be scaled linearly for solar intensity.

Alternatively, the SO_2 rate may be derived from the Gillani et al parameterisation, yielding

$$\text{Rate}_{NO_2} = 0.12 \text{ R.H. } (O_3) \% \text{ hr}^{-1}$$

where

R = Solar intensity (kW m^{-2})

H = Mixing height (m)

(O_3) = background ozone concentration (ppm)

This suggestion carries the caveat that the parameterisation may not be applicable to sites other than those on which it was developed, i.e. LaBadie, Cumberland and Johnsonville. The dark rate constant is again

$$k_2 = 4 \times 10^{-5} \text{ min}^{-1}$$

Procedure III

The rate constant for NO_2 oxidation is estimated from the composition of the reacting air mass, using the correlations between k_2 and adjusted hydrocarbon concentration, or final ozone concentration derived in this work.

If detailed hydrocarbon analyses become available, the former procedure is to be preferred, since, if the ambient hydrocarbon concentration is known, it is simply inserted into the following equation to predict k_2.

$$k_2 = 2.17 \times 10^{-3} + 7.41 \times 10^{-3} \text{ (HC) min}^{-1}$$

where (HC) is the adjusted hydrocarbon concentration given by

$$(HC) = (\text{unsaturated}) + (\text{branched, saturated}) + 1/3\ (\text{unbranched, saturated})$$

(methane is omitted). This equation represents the least squares fit of k_2 to (HC) and the variance of the fit to the above equation was 1.3×10^{-5} min^{-2}, which means that for typical atmospheric conditions we can assign error bars of approximately 0.0035 min^{-1} to k_2. This value for k_2 must be scaled for solar intensity.

In the absence of a detailed knowledge of the hydrocarbon composition it is still possible to obtain an estimate of the adjusted hydrocarbon concentration if it is assumed that the hydrocarbon compositions measured in Los Angeles and St. Louis are generally representative of the hydrocarbon content of polluted atomospheres. (These data were presented by K. L. Demerjian at the 2nd Winter School on Atmospheric Chemistry, Newport Beach, California, in January 1981, but references were not included.)

These compositions are reported in Table 2 and even though the total hydrocarbon concentration in Los Angeles is about ten times higher than that of St. Louis, both yield the result that 1 ppmc is equivalent to 0.154 ppm adjusted concentration.

It is not possible to estimate the error introduced by this procedure but is is probably not worse than that caused by assuming an average rate constant as in procedures I and II above.

Alternatively, for a single plume k_2 can be derived from the approximately steady ozone concentration measured after several hours of plume life. This concentration must be adjusted for dilution caused by plume expansion, since our correlation was obtained from smog chamber results, where no expansion occcurs, and then be inserted into the equation

$$k_2 = 0.0221\ (O_3) - 0.00048\ min^{-1}$$

where (O_3) is in ppm.

This equation results from the least squares fit between k_2 and (O_3), and the statistical fit to the line is approximately the same as for the correlation between k_2 and (HC), so the error bars are again $\pm$ 0.0035 min^{-1}.

As was noted in Section 5, k_2 is subject to a minimun value of 0.0025 min^{-1} during daylight hours, and the recommended night-time value is

$$k_2 = 4 \times 10^{-5}\ min^{-1}$$

6.3. Ratio of HNO_3 to PAN Produced

The division of the products of NO_2 oxidation between PAN and HNO_3 can be obtained from Table 1, using an entry point derived in one of two ways.

i) In smog chamber experiements, Spicer (1979) found a strong dependence of $(PAN)/_{(HNO_3)}$ on $(NMHC)/_{(NO_x)}$, the latter ratio being the initial

one, with NMHC being expressed as ppmC. The points quoted were:

$(PAN)/_{(HNO_3)}$	$(NMHC)/_{(NO_x)}$
4.5	20
2.0	10

and clearly (PAN) = 0 for (NMHC) = 0. These points do not define a linear relationship, but one can be forced within the accuracy of this work, giving

$$(PAN)/_{(HNO_3)} \simeq 0.21\ (NMHC)/_{(NO_x)}$$

Then, if the initial ratio of (NMHC) to (NO_x) is known, $(PAN)/_{(HNO_3)}$ is calculated, then inverted (since Table I is in terms of $(HNO_3)/(PAN)$). This ratio, Y, relates to Spicer's experimental conditions, which correspond to a time of approximately 500 minutes, and a temperature which was not quoted, but is assumed to be 295K. The ratio $(HNO_3)/(PAN)$ at any other time and temperature is then obtained as

$$Y \times \frac{R\ (\text{time, temperature})}{R\ (500\ \text{min, 295k})}$$

where R is read from Table I.

ii) If the initial $(NMHC)/(NO_x)$ is not known, an average $(HNO_3)/(PAN)$ must be assumed for entry into Table I. This can be obtained from Spicer's work on the Philadelphia plume (Spicer & Sverdrup 1979). Measurements taken

there in the summer of 1979 found correlations of HNO_3 and PAN measured at a site where ozone was also measured.

The relationships were

$$(PAN) = -0.0003 + 0.020\ (O_3)$$

$$(HNO_3) = -0.0001 + 0.014\ (O_3)$$

which give an HNO_3 to PAN ratio of 0.70 (ignoring the intercepts as being not significant). This ratio corresponds to a reaction time of about 400 minutes, and a temperature of about 300K. Ratios pertinent to other times and temperatures are obtained as indicated above.

As mentioned in Section 4, the maximum deviation found in the R values was $\pm$ 25%, and this figure can be interpreted as giving the statistical precision of the ratio of HNO_3 to PAN. However, the entry point to the table, i.e. Y, is clearly subject to considerable uncertainty, particularly if (ii) has to be used, and remains as a limiting factor.

6.4. Limits of Applicability of Recommended Rate Parameters

It is very difficult to set down limits to the applicability of the parameters determined in this work, since one is essentially seeking to extrapolate outside the data base. Thus, a smog chamber experiment is only an approximation to what takes place in the atmosphere, while the rate of oxidation of NO_2 in Boston urban plume is only an approximation to what occurs in Ontario.

However, Figure 5 reveals that those atmospheric measurements of k_2 which are available are within a factor of 2.5 of the value predicted by the least squares line and this suggests that the value chosen for k_2 (by whatever procedure) should be reliable to within a factor of 2.5. There remains a need for more, good quality measurements of NO_2 transformation rates in the atmosphere, as well as data on HNO_3 and PAN concentrations, and the findings of this study can be refined in the light of such measurements.

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TABLE I

AVERAGE RATIO, $R = (HNO_3)/_{(PAN)}$, AS A

FUNCTION OF TEMPERATURE AND TIME

TIME/ (min)	265 K	280K	290K	295K	298K	300K	303K
100	0.125	0.133	0.173	0.242	0.339	0.432	0.650
200	0.126	0.145	0.245	0.425	0.658	0.882	1.384
300	0.127	0.159	0.331	0.643	1.029	1.406	2.253
400	0.128	0.173	0.426	0.890	1.452	2.014	3.285
500	0.129	0.188	0.530	1.173	1.935	2.716	4.498
600	0.130	0.201	0.644	1.493	2.487	3.535	5.938
700	0.130	0.220	0.768	1.854	3.116	4.458	7.643
800	0.131	0.237	0.902	2.265	3.834	5.581	9.661
900	0.132	0.254	1.047	2.732	4.653	6.853	12.051
1000	0.133	0.272	1.206	3.263	5.589	8.328	14.881
1100	0.134	0.289	1.379	3.867	6.657	10.040	17.565
1200	0.135	0.307	1.567	4.554	7.876	12.023	22.201

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Table 2. Typical Urban Hydrocarbon Ambient Concentrations During Early Morning Traffic Peak Hours

	Paraffins, ppbC			Olefins, ppbC			Aromatic, ppbC	
	St. Louis	Los Angeles		St. Louis	Los Angeles		St. Louis	Los Angeles
ethane	11	191	ethylene	7	151	benzene	*	90
propane	12	140	propylene	4	60	toluene	23	259
n-butane	16	286	isobutylene	4	47	ethylbenzene	5	48
isobutane	7	65	t-c-2-butenes	4	20	p-xylene	3	48
isopentane	20	312	1,3-butadiene	*	11	m-xylene	3	128
n-pentane	10	171	1-pentene	<1	11	o-xylene	6	64
cyclopentane	9 (	138	2-methyl - 1-butene	1	15	isopropylbenzene	2	27
2-methylpentane	7 (		t-c-2-pentene	<1	32	n-propylbenzene	1	18
3-methylpentane	4	68	2-methyl - 2-butene	<1	29	p-ethyltoluene	4	72
n-hexane	4	82	isoprene	*	*	1,3,5-trimethylbenzene	2	27
2,4 dimethylpentane	5	89	4-methyl - 2-pentene	<1	*	1,2,4-trimethylbenzene	9	81
3,3 dimethylpentane	<1	*	hexenes	<1	15	t-butylbenzene	*	20
cyclohexane	<1	16	Unknowns		9			
2-methylhexane	2	*						
2,3-dimethylpentane	1	*						
3-methylhexane	2	68						
1,3-dimethylcyclopentane	<1	*						
2,2,4-trimethylpentane	1	*						
n-heptane	2	40						
methylyclohexane	1	49						
n-nonane	7	*						
n-decane	2	*						
Unknowns		185						

*Compound not identified/detected in analysis.

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Figure 1: RESULTS FROM PITTS ET AL, UNIVERSITY OF CALIFORNIA, RIVERSIDE

* Best fit to first order (SD = 0.022)

x Worst fit to first order (SD = 0.385)

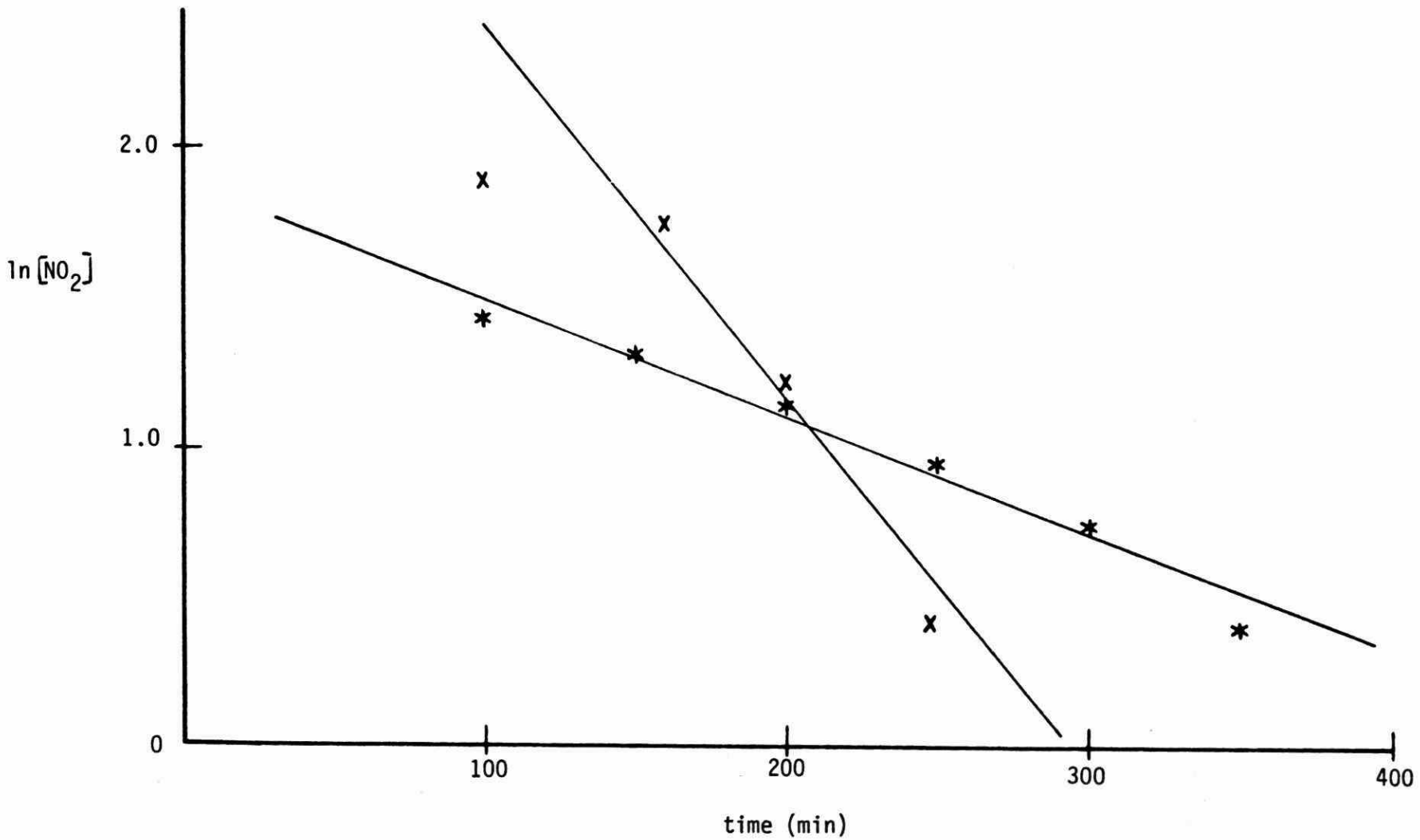


FIGURE 2: RESULTS FROM AKIMOTO ET AL. (Envir. Sci. Technol. 14, 172 (1980)

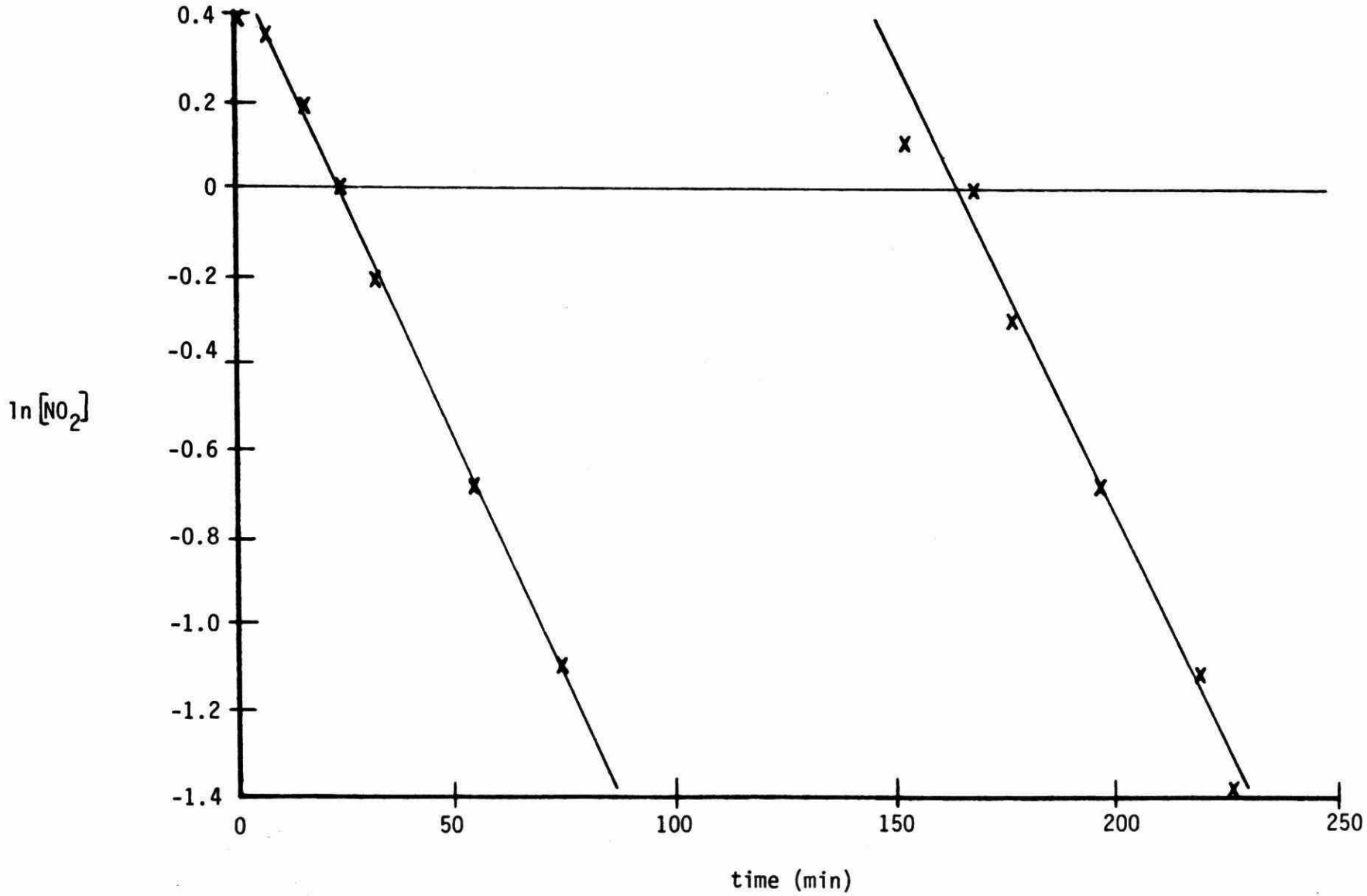


FIGURE 3: CORRELATION BETWEEN k_2 and $[HC]_o/[NO_x]_o$

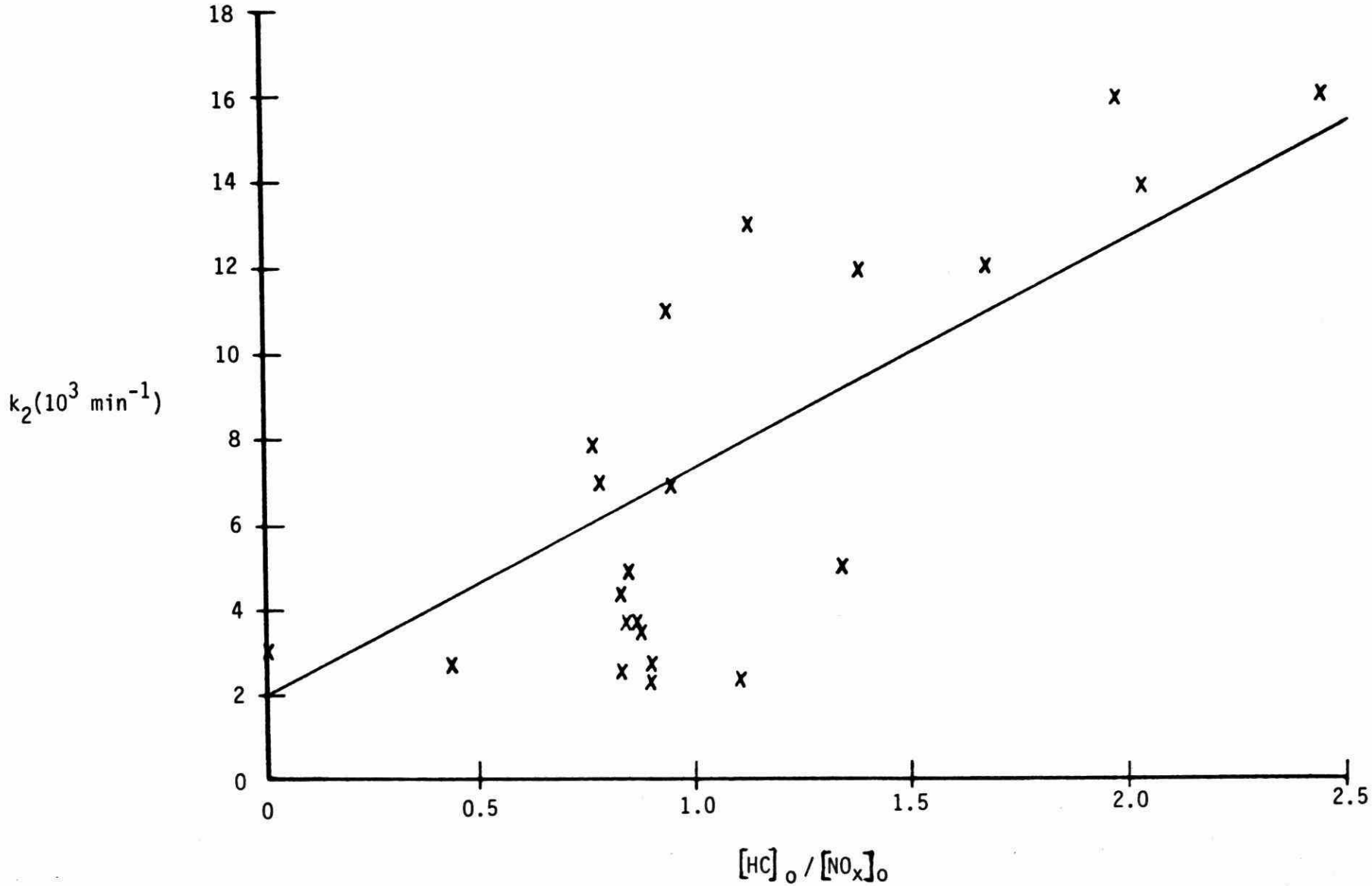


FIGURE 4: CORRELATION BETWEEN k_2 AND INITIAL HYDROCARBON CONCENTRATION (adjusted for reactivity)

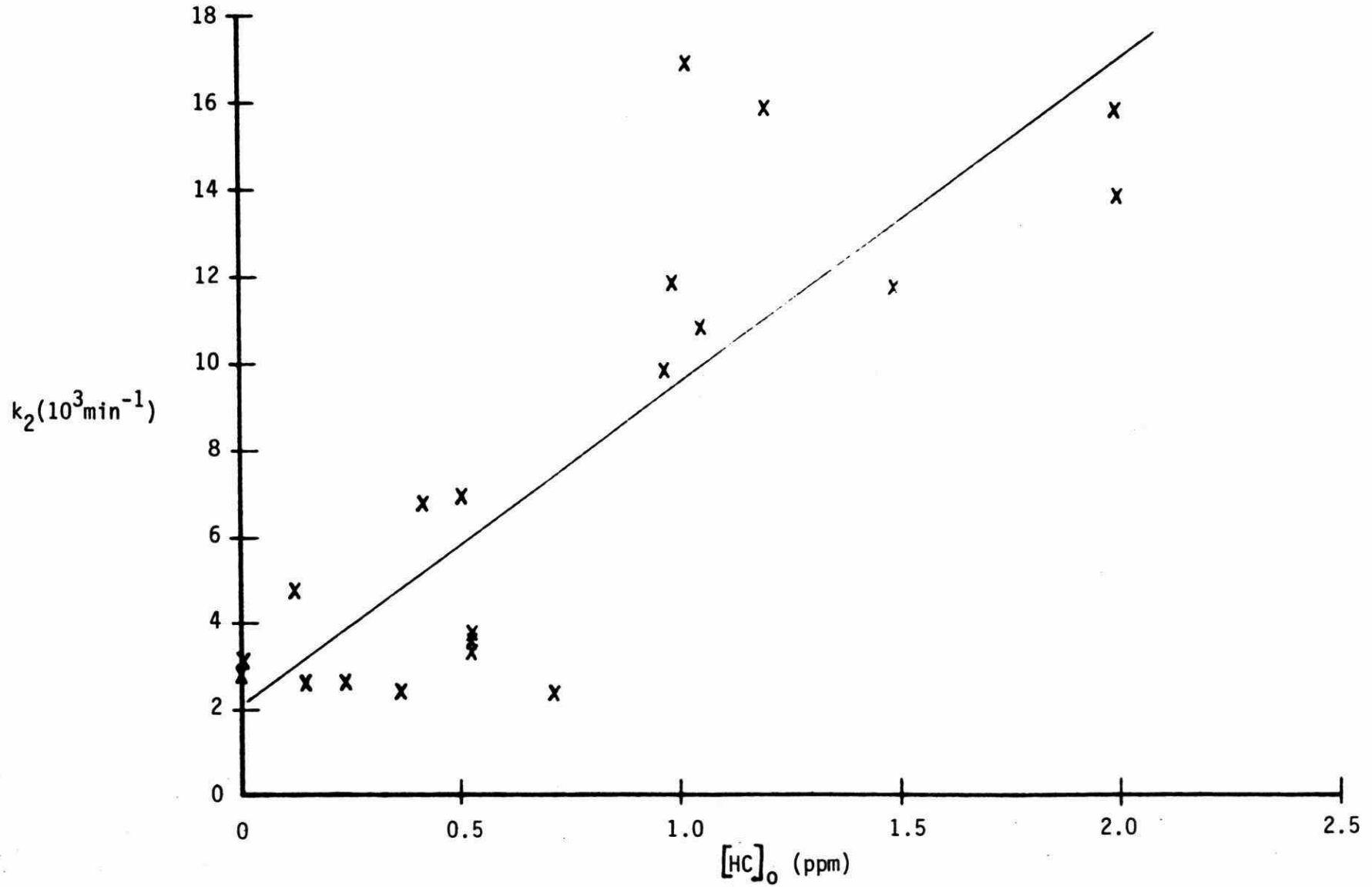
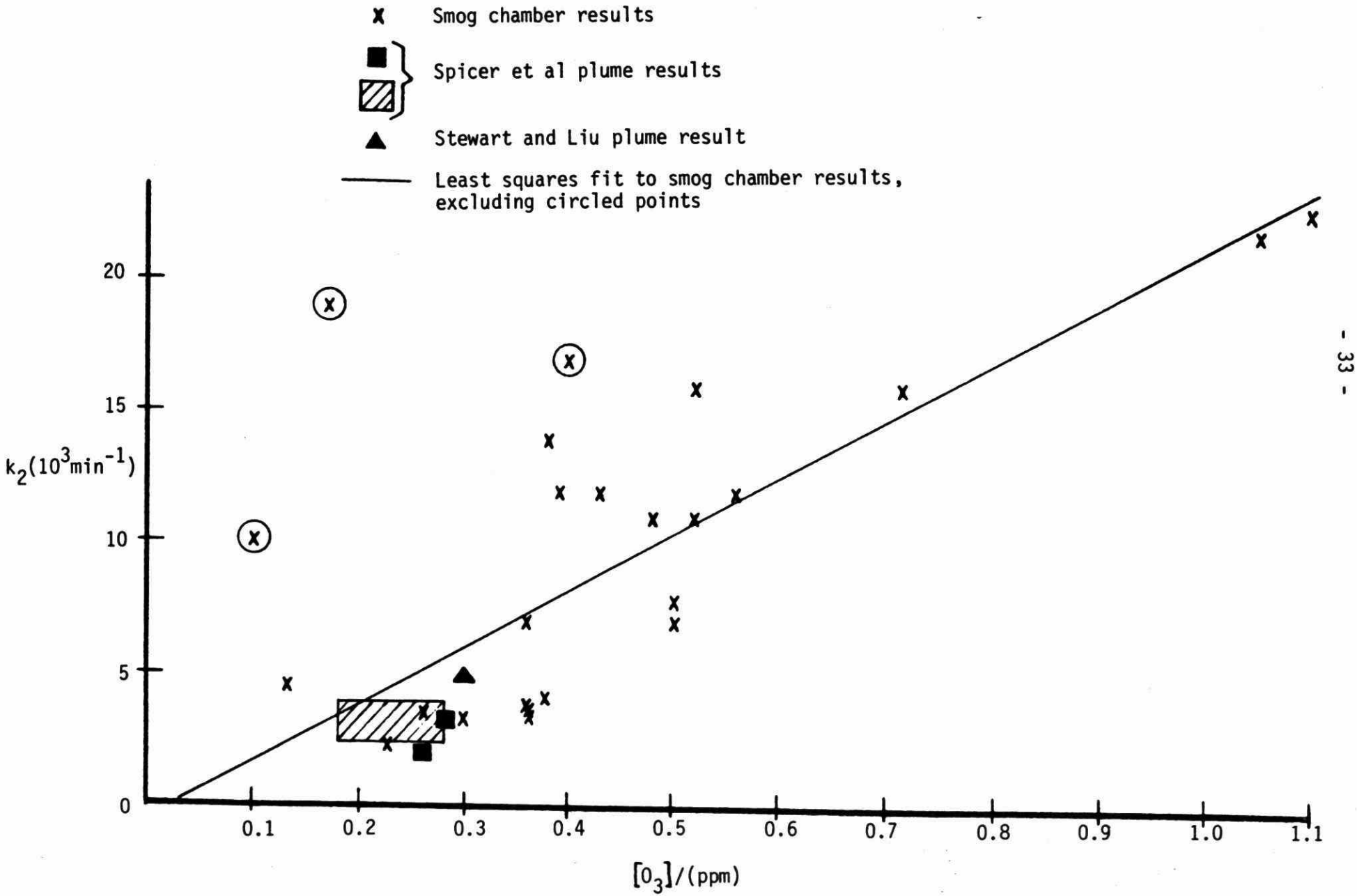


FIGURE 5: CORRELATION BETWEEN k_2 AND FINAL O_3 CONCENTRATION



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